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All three neutralizing agents were capable of treating acid mine drainage. Lime costs were half that of limestone for treating the same acid mine drainage because of the low utilization of limestone. However, the characteristics of the limestone sludge were superior to those of lime and soda ash sludges. The cost for soda ash treatment was excessive. Further research on improving limestone utilization is under way.

No differences in reaction efficiency were found in dry feeding or slurry feeding the neutralizing agents.

Aeration during and/or after the limestone reaction merely increased the effluent pH but failed to increase limestone useage efficiency or improve effluent quality.

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Neutralization of High Ferric Iron Acid Mine Drainage

by

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FEDERAL WATER QUALITY ADMINISTRATION
U. S. DEPARTMENT OF THE INTERIOR

Program 14010 ETV
August, 1970

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This report is for work conducted under Program 14010ETV

Key Words: Neutralization, acid mine drainage, lime, limestone, soda ash, ferric iron, treatment costs, acidity removal, iron removal, pH control.

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CONCLUSIONS

Studies utilizing lime, limestone, and soda ash to treat acid mine drainage having a high ferric/ferrous ratio led to the following conclusions:

1. Lime, limestone, and soda ash can neutralize mine drainage to meet the pH 6.5 - 8.0, net alkalinity, and iron less than 7.0 ppm criteria established by the Commonwealth of Pennsylvania.

2. The major differences between soda ash neutralization and lime or limestone neutralization are that soda ash produces a water low in hardness and calcium and high in sodium. Other chemical parameters are comparable between the three neutralizing agents.

3. Chemical costs for treating by the three methods were: Soda ash - 0.049 cents, limestone - 0.010 cents, and lime - 0.005 cents per mg/l acidity per 1,000 gallons.

4. Limestone sludge is more desirable in that it occupies approximately two-thirds of the volume of lime sludge and has a higher solids content. It contains a large residual alkalinity which would be beneficial when disposed into an acid mine environment (although this residual alkalinity is expensive and of questionable value to the treatment process).

5. Lime is a very reactive material and the neutralization reaction goes to completion in less than a half hour. The limestone reaction requires from 24 to 48 hours to go to completion and therefore, requires a long detention time before discharge, however, aeration will reduce the detention time to one comparable to lime.

6. The limestone reaction is not very sensitive quantitatively, i.e., small changes in limestone feed rate or water quality do not cause large changes in product water quality so the accuracy with which constituents are fed into the reactor need not be controlled with the precision required by lime. Accidental overtreatment is not the pollution problem with limestone that it would be with lime.

7. Lime is capable of attaining higher pH's which may be necessary in some cases for desired water quality, whereas with limestone, pH's above 7.0 are very difficult to attain. In order for the cost of limestone treatment to be competitive with lime, methods of improving the utilization efficiency must be found.

8. For all agents, the majority of the sludge settled in one hour.

9. No difference in the efficiency between dry feed and slurry feed methods of introducing the neutralizing agent was found for lime, limestone, and soda ash.

10. Dry feeding offers fewer operational difficulties than does slurry feeding and costs less, both initially and in cost of maintenance.

RECOMMENDATIONS

The following additional studies are recommended:

1. Enhancement of the limestone process to make it competitive to lime treatment by:

   a. Sludge return to take advantage of the alkalinity within the sludge.

   b. Increasing the detention time in the reactor to allow more limestone to go into solution.

   c. Increasing the shearing action in the reactor to break the calcium sulfate and iron coating of the limestone.

2. Treatment with lime and limestone for increased efficiency, lower cost, and better sludge. It may be possible to utilize the strong points of both the lime and limestone reactions. For example, if limestone were first added to raise the pH from 2.9 to around 5.0 (the most efficient portion of the limestone curve) - Figure 6 - and then use lime to further increase the pH to around 6.5 (the most efficient portion of the lime curve) the resultant might be more desirable than the use of either agent alone. The economics would dictate the final choice of lime-limestone proportions. It is hoped that when the optimum combination is determined, this combination will produce the high pH's characteristic of lime, the low sludge volume of limestone, together with an overall high efficiency and a correspondingly low cost.

3. Development of methods to produce a rapid settling and dense sludge, e.g., the use of coagulating aids.

INTRODUCTION

The Norton Mine Drainage Treatment Field Site, located at Norton, West Virginia, is a research facility of the Federal Water Quality Administration. The field site is situated in the heart of the Appalachian mining fields and conducts research on many phases of mine drainage pollution. Studies on neutralization, treatment by reverse osmosis, reclamation, and mine sealing are now underway and are being evaluated by the Norton staff.

The field site is on the banks of Grassy Run - a small, heavily polluted stream in which an estimated 90 percent of the water flow is from abandoned coal mines. Approximately 70 percent of this pollutant flows directly out of underground mines. In Table I, the water quality of Grassy Run at the Norton site is presented. This water is used as a raw water supply for most treatment studies.

Table I
Grassy Run Water Quality - 1968

Parameter	Units	Max.	Min.	Mean
pH		3.1	2.1	2.8(a)
Specific Conductance	Mmhos/cm	1,800	600	1,190
Hot Acidity (as $CaCO_3$)	mg/l	680	137	466
Calcium (as $CaCO_3$)	mg/l	360	94	211
Magnesium (as $CaCO_3$)	mg/l	140	30	93
Hardness (as $CaCO_3$)	mg/l	470	134	304
Iron (Total)(b)	mg/l	200	10	93
Aluminum	mg/l	70	10	31
Sulfate	mg/l	980	270	612
Flow (Water Year 1968)(c)	cfs	278	1.2	7.52

(a) Median value
(b) Ferric/ferrous ratio greater than 4:1
(c) U. S. Geological Survey data(1)*

The Norton Mine Drainage Treatment Field Site has been conducting a feasibility study of treatment of acid mine drainage using lime, limestone, and soda ash neutralization. The advent of stronger pollution laws and the shortage of reliable at-source pollution control techniques makes treatment a required abatement method. Treatment by neutralization is the most widely used by the industry at this time.

Most mine drainage neutralization research efforts have been with ferrous iron mine water. In contrast, the studies at Norton have concentrated on water with greater than 80 percent ferric iron. There are large areas of the coal region that have mine drainage of the ferric iron type, thus, the need for these studies.

*Numbers in parenthesis refer to references listed at the end of report.

PURPOSES OF STUDY

The specific purposes of this study were:

To investigate the effluent water quality characteristics of high ferric iron acid mine drainage when neutralized to various pH's by three types of neutralizing agents, i.e., lime, limestone, and soda ash.

To compare the effectiveness of each of the three neutralizing agents in neutralizing acid mine drainage to various pH's.

To determine optimum basic operating conditions required to neutralize acid mine drainage in order to produce an effluent water which would meet state standards.

To acquire relevant operating data at the optimum conditions, derived from actual pilot plant operation.

To enhance the efficiencies, if possible, of the limestone neutralization of acid mine drainage.

PILOT PLANT FACILITIES

Plant Layout

A simplified flow diagram of the pilot plant neutralization system is presented in Figure 1.

Water from Grassy Run was pumped into a 500 gallon fiberglass tank which was kept constantly full by allowing continuous overflow. This tank served as a constant head source from which water was gravity fed at a constant rate into the reactor. Flow rates from the tank ranges from 1-6 gallons per minute. Control of this flow was accomplished by means of a globe valve (other type valves fouled or allowed the flow rate to vary excessively). The reactor was a 55 gallon stainless steel tank on which a flash mixer was mounted. Into the reactor, a neutralizing agent could be fed in either the dry or slurry form. The dry feeder used was a volumetric type disc feeder which performed reliably and had an observed feed accuracy of ± 2 percent. The slurry feed system consisted of a storage tank exactly like the reactor tank with a flash mixer. Constant agitation was supplied by the mixer to keep the relatively insoluble neutralizing agent in suspension. Small precise chemical feed pumps were used to transfer the slurry from the slurry storage tank into the reactor. These pumps were electrical solenoid type, rapid impulse, diaphragm pumps chosen for their ability to pump the heavy slurry accurately.

The reactor contained a pH probe for a recording pH meter. This meter was used for precise monitoring and control of the system.

Water level in the reactor was maintained by float switch controlled pumps which transferred the neutralized water from the reactor into a 1,250 gallon upflow settling tank.

Supernatant from the settling tank, which was considered treated water, overflowed into a sampling line and returned to Grassy Run. The sludge from the settling tank could be either periodically or continually withdrawn (depending upon the length of the test run) and was transferred to a holding pond for periodic disposal.

The presence of a pressurized rapid sand filter in the flow system was to remove all large particulate matter which, at low flow rates and the correspondingly small orifices in the valves, tended to clog the valves and thus vary the flow.

The necessity for filtration appeared to decrease with respect to increased flow rates and valve clearances. Thus, filtration would not be as necessary in full scale plants or large pilot plants.

Detention Time Study

Studies were initiated to determine the detention time in the settling tank and reactor. A number of tracer techniques were used to determine

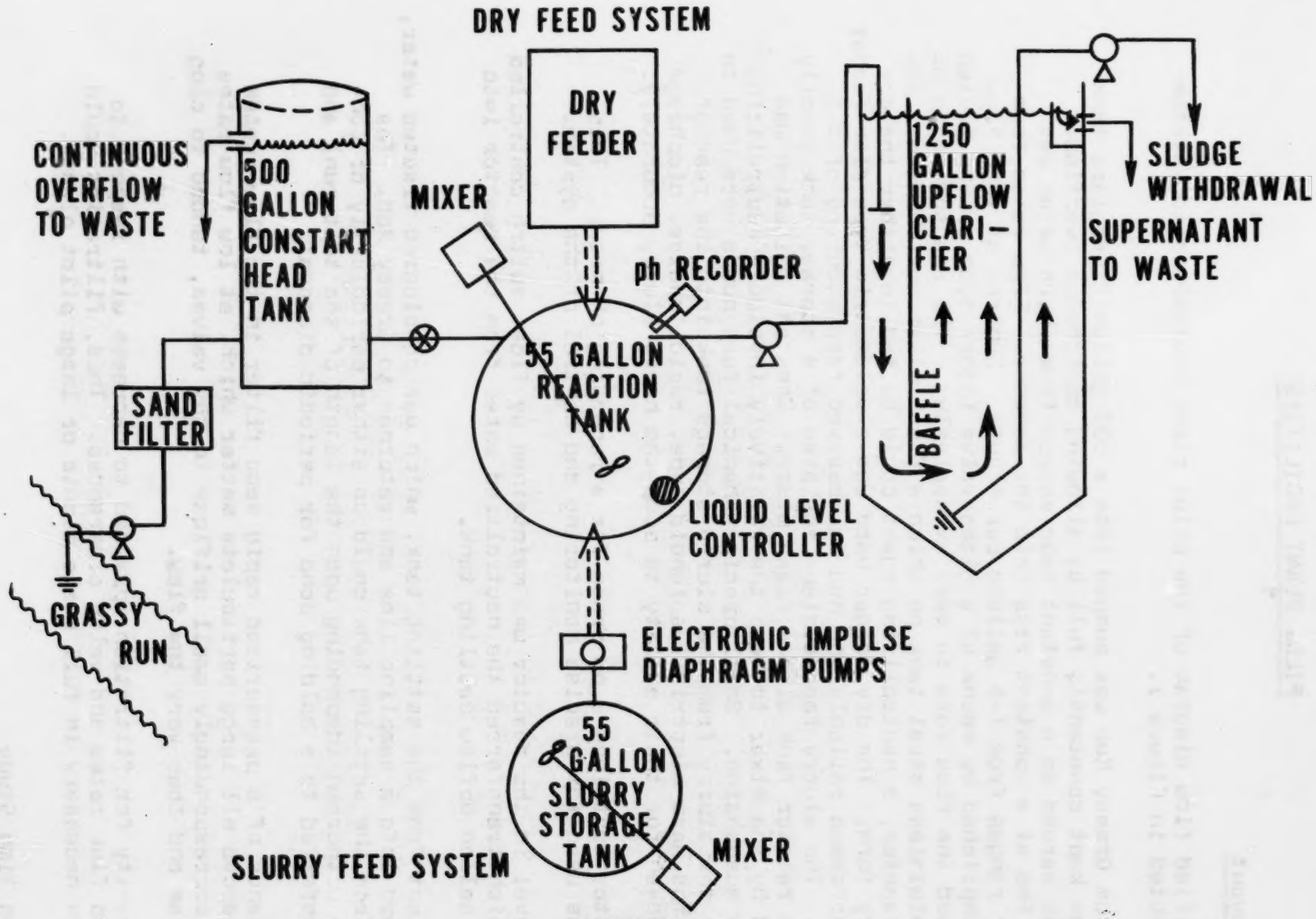

FIGURE 1
SIMPLIFIED FLOW DIAGRAM

detention time and to evaluate modifications of the equipment. The most effective tracer was NaCl.

For the reactor detention time test, a strong salt solution (NaCl) was injected instantaneously into the reaction tank which was full of tap water and operating at an inflow-outflow rate of 2.66 gpm. The flash mixer was operating to form a vortex in the reactor. Conductivity readings were taken at one minute intervals at the reactor discharge. Forty minutes were required for the salt to pass through the reactor as shown by the conductivity returning to its initial reading. As the capacity of the reactor was 44 gallons, the theoretical detention time was 16.5 minutes. (Volume of tank, gals./ flow rate, gpm). Evidence of rapid mixing is illustrated by the peak of the conductivity curve (Figure 2) occurring 30 to 45 seconds after the addition of the NaCl. A logarithmic probability plot of the data indicated that the average detention time was 5.7 minutes. Thus, the efficiency of the reactor (Mean probably detention time X 100/theoretical detention time) was 34.8 percent.

From visual observations it was evident that the upflow settling tank suffered from short circuiting and that modification of the tank was required (Figure 3). A baffle was constructed near one end of the tank which caused the water to flow more evenly into the bottom. In addition, the overflow was changed from a pipe to a trough outlet. Tracer tests performed on the modified tank are presented in Figure 4. These tests were made by instantaneously injecting the NaCl solution into the input line of the tank which was being operated at 4.5 gpm rate. As the tank capacity was 1,250 gallons, the theoretical transit time was 4.6 hours. It required 9.0 hours for the conductivity at the settling tank discharge to return to a base level. A logarithmic probability plot showed the average detention time to be 3.70 hours, indicating an efficiency of 80 percent.

Operational Procedures

Normal operational procedures during a test run of the system involved the following:

As pH was the only meaningful parameter that could be continuously and immediately monitored, pH was used for operational control. The raw water flow was controlled by the globe valve which maintained a constant flow of feed water into the reactor throughout the test run. By adjusting the chemical feed rate, a constant pH was established in the reactor. Samples were taken from the reactor after a few hours operation when the system had come to equilibrium. However, several days of operation were required to allow the formation of an active sludge blanket in the settling tank before the effluent was sampled. Once the sludge blanket was established, normal sampling procedures were begun. Samples were taken from the inflow (raw Grassy Run water), treated water (immediately from the discharge of the reactor) and from the settling tank effluent. Rates of the raw water inflow and neutralizing agent feed were measured and the

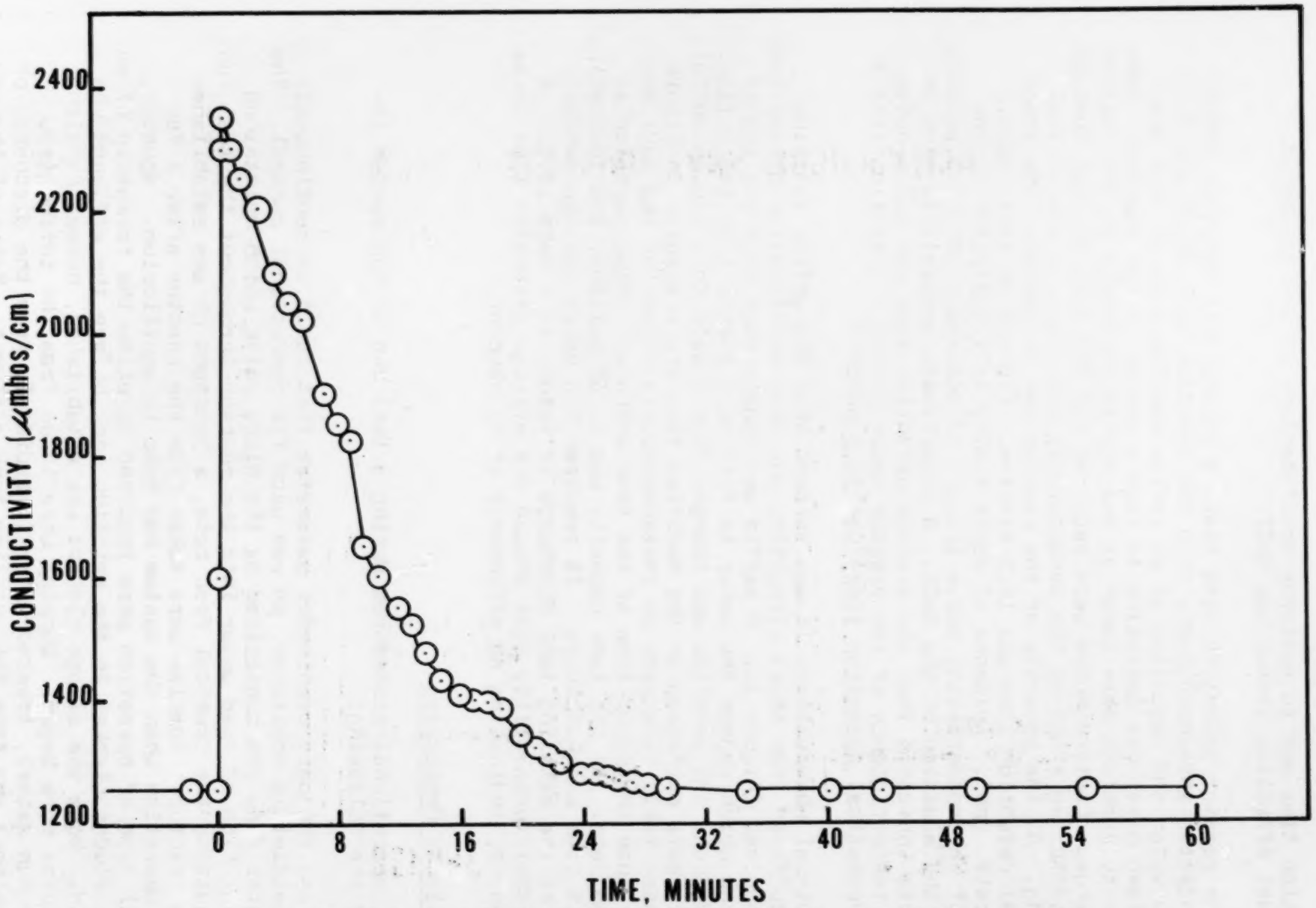

FIGURE 2 DETENTION TIME STUDY—REACTOR TANK

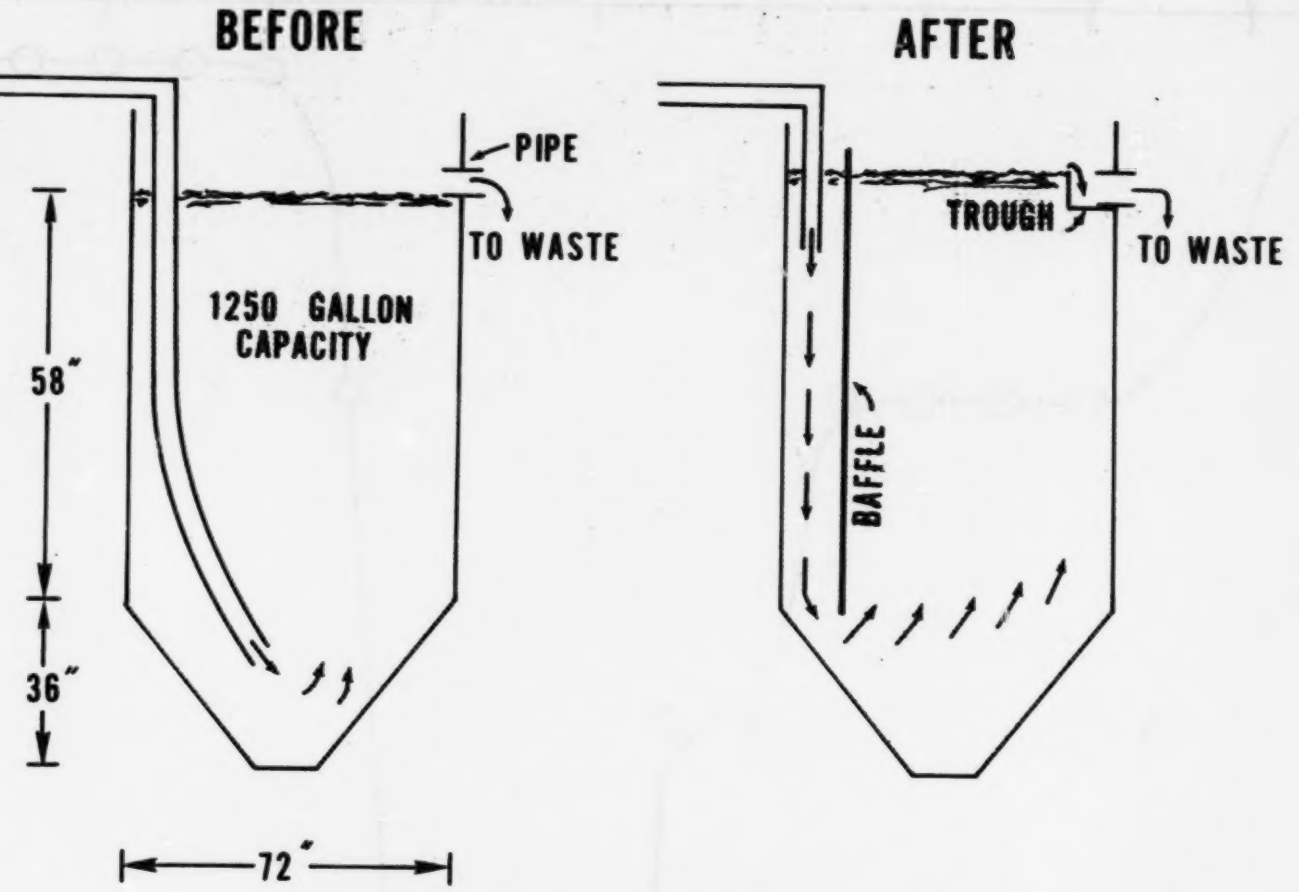

FIGURE 3 SETTLING TANK MODIFICATION

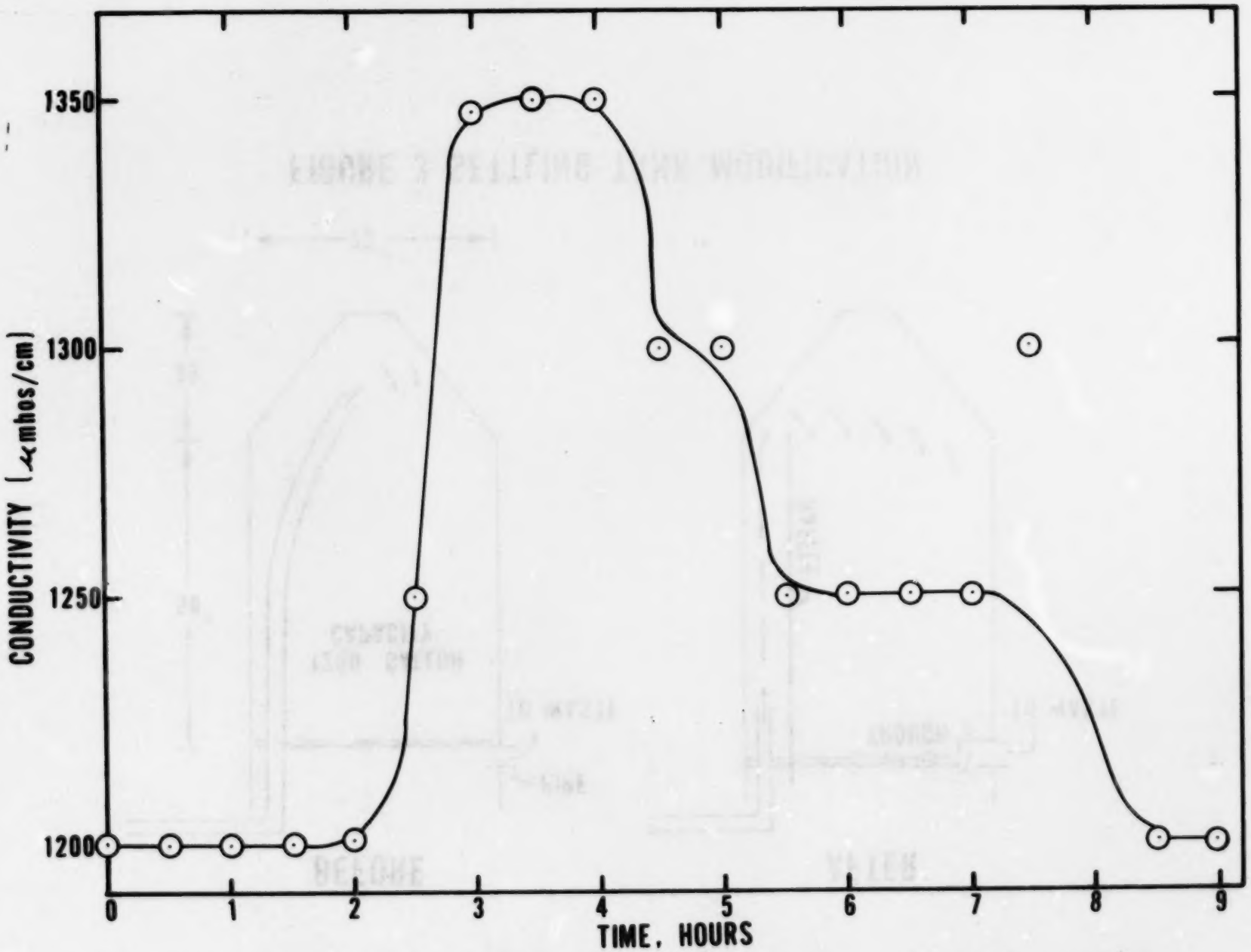

FIGURE 4 DETENTION TIME STUDY – SETTLING TANK

temperatures of all three water samples were recorded. A sample was also taken to measure the sludge settling rate and volume. This sample of treated water was taken from the reactor discharge and placed in a 1,000 ml graduate. The height of the precipitated sludge was recorded every fifteen minutes for a period of one hour. In a few cases, long term settling tests were made with periodic readings up to 24 hours and longer.

When the slurry feed method of introducing the neutralizing agent was used, the slurry mixture was prepared on a batch basis in a separate tank and then dumped into the slurry storage tank. A flash mixer constantly agitated the slurry to keep the relatively insoluble neutralizing agent in suspension. Electronic impulse diaphragm pumps, whose flow could be varied electronically, transferred the slurry into the reactor. Even with these specialized pumps, a five percent (by weight) limestone slurry was the maximum concentration (of limestone) the pumps were able to transfer. Although lime slurries were much easier to keep in solution (as calcium hydroxide is much more soluble than calcium carbonate), fouling problems were also experienced with it. Studies were not performed on soda ash slurries.

When the dry feed method of neutralization was used, control of the neutralizing agent feed rate was accomplished by adjusting a variable speed transmission on the dry feeder.

During aeration studies in the reactor, a 3/4 inch PVC plastic pipe 'U' was inserted in the reactor tank. The sides of the 'U' fit vertically against the sides of the reactor tank and the bottom of the 'U' laid near the bottom of the tank. The bottom of the 'U' was drilled with a number of 1/16 inch holes spaced to provide an equal distribution of air throughout the reactor.

When aeration of the settling tank was studied, a rectangular aerator, made from four lengths of 3/4 inch PVC piping, was suspended above the sludge blanket. Holes 1/16 inch in diameter were drilled in the rectangular aerator and spaced to provide maximum dispersion. Sufficient air pressure was used to maintain vigorous agitation of the supernatant. Initially, the rectangular aerator was placed eight inches above the sludge blanket, but the turbulence disturbed the blanket. The aerator was then moved to a height of 15 inches above the blanket.

PROCEDURES

Before pilot plant studies were conducted, it was necessary to develop test procedures. A study was undertaken to determine the best time for analysis of samples, to determine the characteristics of the neutralizing agents, and to determine the chemical requirements to reach a specific pH. These studies are reported here.

Analytical Procedures

As pH was found to vary with time following neutralization and as the solubility of metal salts in the water is dependent upon pH, it was critical to establish a standard time of analysis following neutralization.

A study of pH change following neutralization was conducted to determine the optimum time for analysis. Samples of acid mine water were neutralized and agitated by flash mixers for 10 minutes. Then the samples were allowed to set undisturbed and the supernatant pH's were periodically recorded. Figure 5 indicates the pH change with time after the addition of lime, limestone, and soda ash to identical samples of acid mine drainage.

In the case of lime, the reaction was rapid and the pH was stabilized after a half hour, thus indicating that the reaction had gone to completion. However, when limestone was the neutralizing agent, the pH had not stabilized even after 96 hours. In the case of soda ash, the pH change curve closely resembles the limestone curve and the water required a comparable time to come to a stable condition.

After considering these results, the standard procedure of analyzing samples just prior to 24 hours after sampling was adopted. At this time, the lime reaction had gone to completion and the limestone and soda ash reactions have had what we felt to be the maximum detention time which would be found in any operational neutralization plant.

Characteristics of Neutralizing Agent

The importance of particle size in the neutralization reaction has been emphasized in studies by Ford, Young, and Glenn,[3] which indicated that decreasing the particle size of limestone increases both the speed and efficiency of the neutralization reaction. They recommend a particle size of 400 mesh or smaller. Ford and Young tested 13 limestones from the Eastern United States and rated the limestone used during these studies (Germany Valley Limestone Company) as the most efficient in reference to reactivity with acid mine drainage. A spectrochemical analysis of this limestone was made by Bituminous Coal Research and is presented in Table II.

Sieve analysis were made on the three neutralizing agents used. These size determinations were made on a standard sieve shaker with

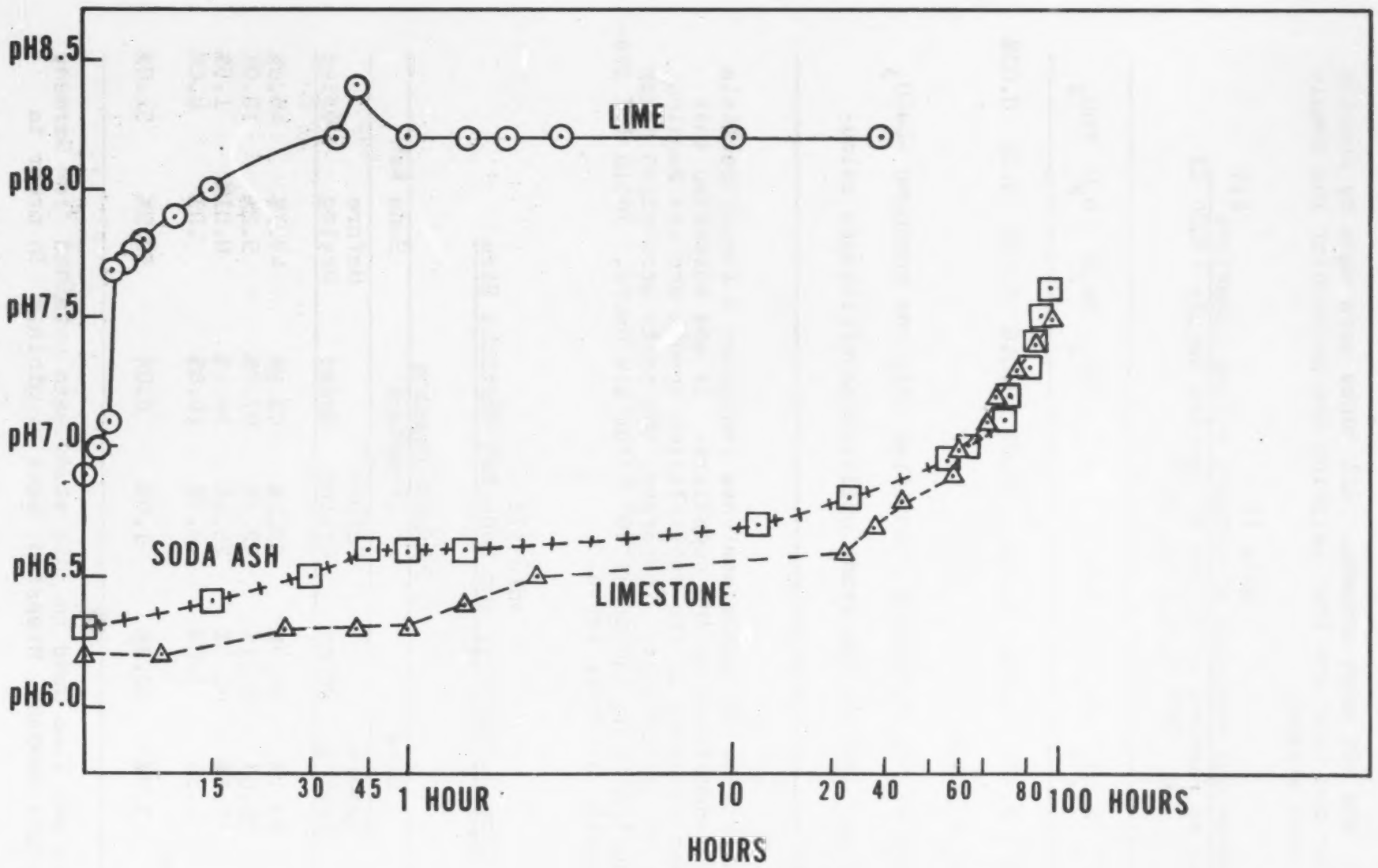

FIGURE 5
"pH CHANGE FOLLOWING NEUTRALIZATION"
(samples taken immediately from reactor)

50, 100, 200, and 400 mesh screens. All tests were made by shaking the sample for one hour and then weighing the portion of the sample retained on each screen.

Table II
Spectrochemical Analyses of Germany Valley Limestone[3]
Reported as Percent by Weight of Ignited Sample (900° C)
BCR Sample No. 2177

Loss on Ignition	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	TiO_2	Na_2O	K_2O	MnO_2
43.0%	1.0%	0.43%	0.15%	1.16%	97.0%	0.04%	0.02%	0.1%	0.03%

Percent $CaCO_3$ = 96.5%*

X-Ray analysis of the limestone identified only one compound -$CaCO_3$

*This figure was used in limestone utilization efficiency calculations as P.

Initial results from the sieve analyses indicated a larger particle size than was advertised by the suppliers. It was suspected that water had been absorbed by the neutralizing agents and was causing the material to agglomerate. Therefore, the tests were rerun after drying the neutralizing agents at 90° F for six hours. Table III presents the results of these tests.

Table III
Lime, Limestone, and Soda Ash Particle Size

	Percent Passing					
	Lime		Limestone		Soda Ash	
Screen Size	Before Drying	Dried	Before Drying	Dried	Before Drying	Dried
50 Mesh	92.1%	89.7%	98.1%	99.2%	49.1%	49.0%
100 Mesh	36.0%	55.1%	42.2%	57.7%	9.2%	10.0%
200 Mesh	5.6%	43.5%	26.6%	34.4%	0.01%	1.5%
400 Mesh	1.5%	3.8%	4.5%	14.8%	.0%	0.6%
% Not Passing 50 Mesh	7.9%	10.3%	1.9%	0.8%	50.9%	51.0%

The limestone and lime used in this study were obtained from Germany Valley Limestone Company, Riverton, West Virginia.* In order to

*Mention of commercial products does not imply endorsement by the Federal Water Quality Administration

obtain the smallest particle size commercially available at a reasonable cost, the 'rock dust' form of limestone was used. The soda ash is from Diamond Shamrock Corporation, Cleveland, Ohio.*

In Table IV, the chemical analyses as quoted by the manufacturers are presented along with the respective cost of the chemical.

Table IV
Manufacturer's Chemical Analyses of Neutralizing Agents

Hydrated Lime		Limestone		Soda Ash	
CaO	72.00% Min.	CaO	53.0%	Na_2O	58%
MgO	00.40% Min.	MgO	0.38%	Na_2CO_3	99-100%
$CaCO_3$ Equivalent	130% Min.	$CaCO_3$	98.8%		
		SiO_2	0.49%		
		Cost			
$17.00 per ton in bags		$6.00 per ton in bags		$100.00 per ton in bags	

Concentration vs. pH Tests

Tests to indicate the relative concentrations of the chemical constituents at various pH's were run by the following procedure: First, a five gallon sample of water from Grassy Run was taken into the lab and allowed to reach ambient temperature. The water was then divided into one liter portions. A separate sample was used for each pH point in the test. The neutralizing agent was added to the sample in sufficient quantity to bring the sample to the desired pH. A laboratory flash mixer was used to agitate the sample. Once the pH had stabilized, the supernatant was withdrawn and analyzed. As discussed earlier, the time required for pH stabilization was dependent on the neutralizing agent used. A 24-hour maximum limit was placed upon the reaction times, thus the limestone and soda ash pH readings and supernatant analyses were made at the 24 hour point. By running all the solubility tests from one large water sample, many variables were eliminated and direct comparisons could be made between the results of each of the three neutralizing agents.

Chemical Analytical Procedures

Cold acidity was measured at 25° C by automatic potentiometric titration to an end point of pH 8.3. Hot acidity was done by potentiometrically titrating a boiling sample to an end point of pH 8.3. Iron, aluminum, calcium, and magnesium determinations were by atomic absorption spectrophotometry. Hardness was the summation of calcium

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and magnesium. "Standard Methods"[2] were used for the alkalinity, total residue, and sulfate determinations. The supernatant was used for these analyses rather than the total sample.

Sludge alkalinity and total residue were determined by "Standard Methods"[2] procedures.

Utilization Efficiency

In order to compare the different methods of neutralization, the efficiency of usage of each chemical was computed. This Utilization Efficiency was defined as the ratio of neutralizing agent used/neutralizing agent added. This concept includes not only the alkalinity used to counteract acidity, but also includes the excess alkalinity imparted to the supernatant. It was felt that a benefit was derived from not only the acidity removed but also the alkalinity added to the water. The alkalinity precipitated with the sludge was considered a loss. Therefore, the formula for determining efficiency was:

$$\text{Utilization Efficiency (Percent)} = (H + A) \times 100/(N \times P)$$

Where H = Hot Acidity Removed (as $CaCO_3$), mg/l
A = Alkalinity of Supernatant (as $CaCO_3$), mg/l
N = Neutralizing Agent Used ($CaCO_3$ equivalent), mg/l
P = Purity of Neutralizing Agent, Percent

RESULTS

Concentration vs. pH Tests

Tests were run on identical samples of Grassy Run water to determine the quality of the supernatant when the sample was neutralized to various pH's. Lime, limestone, and soda ash were each tested as the neutralizing agents. The results of the tests are presented in Table V.

When lime was used, the acidity was removed between a pH of 4.6 and 5.0. At this pH, the iron, sulfate, and aluminum had been decreased to values near minimum levels and the calcium, hardness, and magnesium had increased as a result of the lime addition. It was not until a pH of 9.2 that the magnesium was reduced to a low level. The addition of more lime, beyond a pH of 5.9, served only to increase the pH and decrease the magnesium since there were no further significant increases in the alkalinity or calcium concentrations. Thus, above pH 5.9, the lime was being lost to the sludge. It should be noted that the iron and aluminum were never reduced below 2 mg/l. Referring to our definition of utilization efficiency, it can be seen that the greatest efficiency would be obtained between a pH of 4.6 and 5.0, because at this pH the demand by the acidity had been satisfied. When more lime was added, at first a small amount was used to increase the alkalinity and the rest was lost to the sludge. Eventually all of the further addition of lime would be lost to the sludge.

In these tests, limestone was not able to increase the pH beyond 6.5, because of the formation of carbonic acid which acted as a buffer. An indication of the carbonic acid is seen in the difference between the hot and cold acidity. The difference is mostly due to carbonic acid which is driven off during heating. At a pH of 3.9, the hot acidity was removed but it wasn't until pH 5.5 that the iron was reduced to a minimum of 2 mg/l. Aluminum reached its minimum at pH 4.3. Greatest utilization efficiency, as defined in this report, occurred at pH 3.9. Above this pH, some of the limestone is utilized to increase the alkalinity, but the majority is lost to the sludge.

Soda ash removed all the acidity at a pH slightly above 4.7. The carbon dioxide liberated during the reaction caused the continued presence of cold acidity. Although iron results were erratic, it can be concluded that a concentration of approximately 3 mg/l is the minimum value. Aluminum reached its minimum at approximately 2 mg/l at pH 5.4. Continued increase of soda ash addition beyond pH 4.7 served primarily to increase the pH, alkalinity, and sodium concentration. Maximum utilization efficiency occurred at pH 4.7.

One of the pronounced results of these concentration tests was the continued presence of iron, even at high pH levels. This presence of iron is in contrast to published 'ideal' concentration curves, such

Table V

Composition of Acid Mine Drainage at Various pH's After Neutralization

pH	Conductivity	Hot Acidity	Calcium	Magnesium	Total Hardness	Cold Acidity	Sulfate	Iron	Aluminum	Alkalinity	Sodium
					RAW WATER						
2.8	1,300	594	396	174	570	680	1,542	130	44		2.0
					LIME						
3.5	1,100	261	816	180	996	300	1,192	10.6	40		3.9
3.8	1,060	168	938	182	1,120	205	1,192	4.3	34		2.9
4.2	1,060	34	1,031	185	1,216	50	1,205	3.0	7		2.7
4.6	1,100	2	1,181	185	1,366	0	1,156	2.8	1.6	6	3.0
5.0	1,100	0	1,181	182	1,363	0	1,180	8.5	3.1	14	2.7
5.3	1,100	0	1,181	170	1,351	12	1,192	4.3	3.2	20	3.3
5.6	1,100	0	1,266	167	1,433	7	1,180	5.5	4.0	22	3.1
5.9	1,100	0	1,312	152	1,464	0	1,192	4.9	4.6	30	2.7
6.1	1,100	0	1,312	144	1,456	0	1,192	3.7	4.2	38	3.0
6.4	1,100	0	1,312	142	1,454	0	1,192	2.5	4.1	30	3.2
6.7	1,100	0	1,312	134	1,446	0	1,192	2.4	3.9	32	2.8
7.0	1,100	0	1,312	113	1,425	0	1,192	2.7	3.3	32	2.8
7.3	1,100	0	1,500	52	1,552	0	1,192	3.0	2.7	30	3.4
8.3	1,100	0	1,500	16	1,516	0	1,192	3.3	2.8	36	3.2
9.2	1,100	0	1,575	8	1,583	0	1,180	2.5	3.5	40	3.3

Table V (Continued)
Composition of Acid Mine Drainage at Various pH's After Neutralization

pH	Conductivity	Hot Acidity	Calcium	Magnesium	Total Hardness	Cold Acidity	Sulfate	Iron	Aluminum	Alkalinity	Sodium
					LIMESTONE						
3.6	1,160	24	890	178	1,068	269	1,132	5.8	36		2.4
3.9	1,100	0	998	179	1,177	160	1,144	5.5	24		3.2
4.3	1,100	0	1,096	179	1,275	35	1,156	4.5	2.6		3.1
4.8	1,200	0	1,331	182	1,513	16	1,192	3.3	2.1	44	2.9
5.0	1,200	0	1,500	185	1,685	8	1,192	4.1	2.2	58	3.1
5.5	1,200	0	1,181	185	1,366	11	1,084	1.9	1.9	64	3.1
6.5	1,200	0	1,235	192	1,427	12	1,110	2.0	2.0	71	3.1
					SODA ASH						
3.1	1,200	240	422	178	600	320	1,156	10.0	42		165
3.5	1,200	172	404	179	583	251	1,192	5.5	38		204
4.0	1,200	68	401	179	580	95	650	7.2	16		320
4.7	1,300	2	401	182	583	22	1,301	7.4	2.9	14	330
5.4	1,500	0	401	182	583	26	1,638	3.7	2.3	120	450
5.8	1,600	0	375	182	557	47	1,783	10.6	4.0	166	495
6.2	1,600	0	375	185	560	30	1,638	4.6	2.3	140	510
6.5	1,700	0	372	179	551	11	1,350	5.0	2.4	220	645
6.9	1,700	0	355	176	531	27	1,638	10.0	3.9	246	690
7.3	1,700	0	332	172	504	0	1,687	2.6	2.3	320	750
7.6	1,700	0	315	170	485	0	1,422	2.8	2.5	284	1,000
8.3	1,700	0	232	164	396	0	1,398	2.7	3.0	220	1,000
9.0	1,700	0	161	154	315	0	1,350	2.8	3.9	316	960
9.6	2,800	0	58	123	181	0	1,156	3.0	7.3	1,028	1,460

All units are mg/l except Conductivity (Mmhos/cm) and pH
* All analyses made after 24 hours.

as those by Hill[4] which indicate complete ferric iron removal above pH 5.0. Similar difficulties in iron removal have been reported by Maneval, at al.[5]

Since the analyses were made on unfiltered samples, it was suspected that possibly the iron was remaining in suspension rather than in solution. Therefore, three samples were analyzed for iron, then filtered through a 0.45 micron filter to remove all particle matter and the iron analysis was repeated. The results of this test are in Table VI. Obviously, the iron concentration was not affected by filtration, thus the iron does not exist in a suspended particle state unless it is smaller than 0.45 microns. The iron may be involved in an organic complex. However, no studies have been made to resolve this question.

Table VI
Effect of Filtration
Upon Iron Concentration

Suspect Sample	pH	Total Iron Concentration	
		Before Filtering	After Filtering
L-6	7.0	6.7	6.6
L-7	7.3	10.1	10.2
L-8	8.0	17.2	17.1
L-9	10.0	2.0	2.0

Filter Size = 0.45 microns

Relative Reactivity Study

The relative reactivities of lime, limestone, and soda ash were compared by the addition of measured amounts of each neutralizing agent to identical separate samples of Grassy Run water. Graphs of the results of these tests are shown in Figure 6. These tests were run allowing five minutes reaction time between incremental addition of the neutralizing agents.

In the lime reaction, the steep slope between pH 4.0 and pH 8.0 is indicative of the quantitative sensitivity of the lime reaction in this portion of the curve. It is obvious that a very small change in the amount of lime added at pH 6.0 can easily shift the pH one to two full points. Thus, in the lime reaction, accuracy of feed is of vital importance.

The slope of the limestone curve decreases rapidly at pH's above 6.0 as the reaction liberates CO_2 which, in turn, buffers the reaction. Consequently, the curve is nearly flat above pH 7.0 and increases in pH above this point are very difficult to attain. However, the shallow slope of the curve in the pH 5.0 - 7.0 range would make the

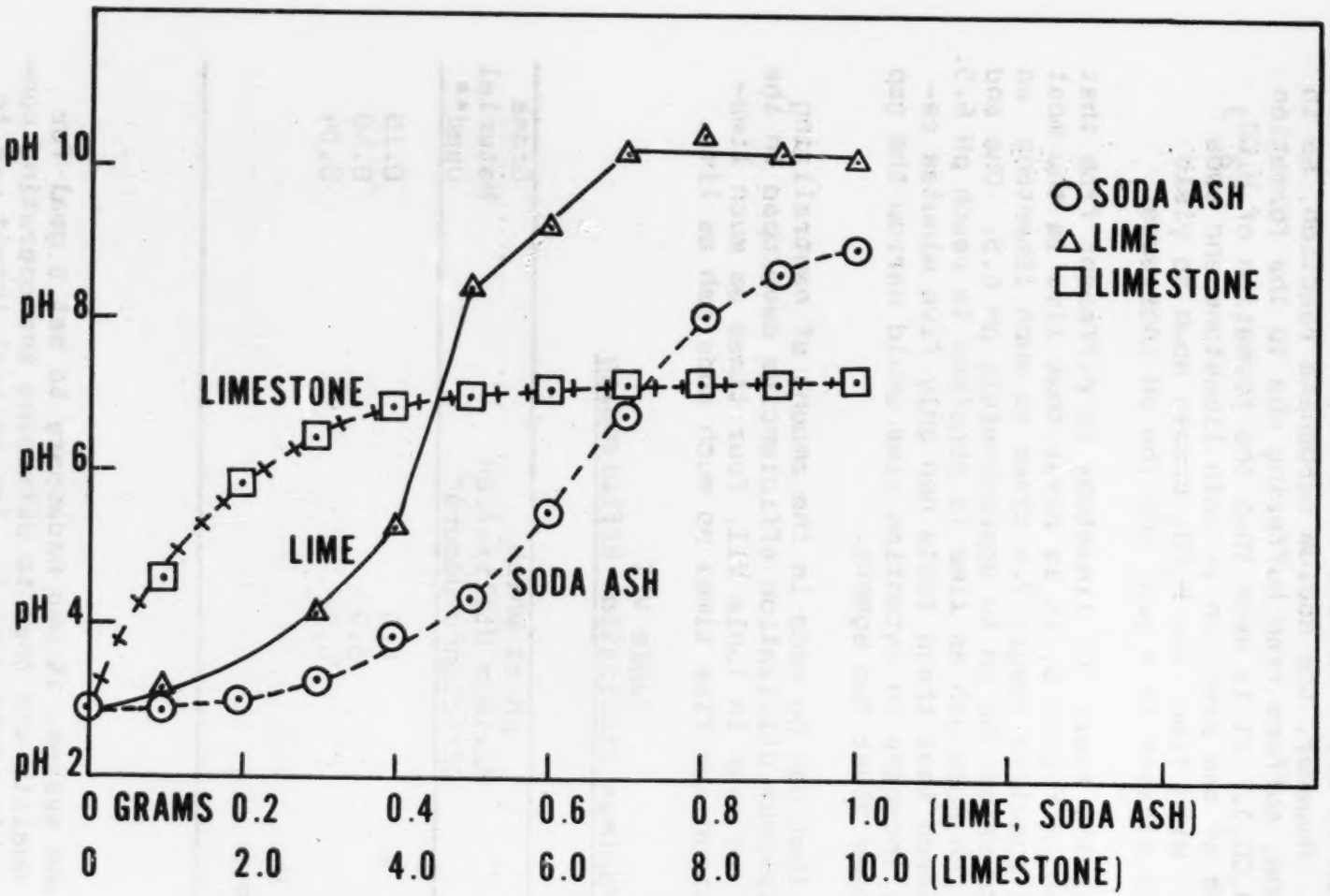

FIGURE 6
COMPARISON OF LIME, LIMESTONE, AND SODA ASH REACTIVITIES

limestone reaction an easy one to control in an operating system as the reaction would be insensitive to small changes in the neutralizing feed rate.

The soda ash reaction is quite similar to the lime reaction in the shape of the curve. However, the sodium carbonate reaction, as in the case of limestone, suffers from buffering due to the formation of carbonic acid (H_2CO_3). It is seen that the formation of H_2CO_3 retards the progress of the reaction in both limestone and soda ash neutralization. With time, the H_2CO_3 breaks down to yield carbon dioxide which escapes as a gas, and the pH increases.

Keeping in mind that the scale for limestone is different from that of lime and soda ash in Figure 6, it is clear that lime is the most reactive agent. It requires rougly 7.4 times as much limestone as lime in this case to raise the pH to approximately pH 6.5. One and one-half times as much soda ash as lime is required to reach pH 6.5. It should be remembered that these tests had only five minutes reaction time and any increase in detention time would narrow the gap between lime and these other two agents.

Another comparison that can be made is the amount of neutralizing agent used at the maximum utilization efficiencies developed in the preceding section. As seen in Table VII, four times as much limestone would be required and five times as much soda ash as lime.

Table VII
Maximum Utilization Efficiencies

Neutralizing Agent	pH at Which Maximum Utilization Efficiency Occurs*	Grams Material Used**
Lime	4.6	0.10
Limestone	3.9	0.40
Soda Ash	4.7	0.54

* Data from Table V
** Data from Figure 5

Optimization

Before optimizing the system, it was necessary to set a goal for the effluent water quality and then to determine the operating conditions which best achieved this goal. The initial intent was to produce the best effluent possible. Considerations of cost paled this view somewhat to the more realistic criteria of meeting and/or exceeding the water quality standards of the mining states which, in themselves, proved quite restricting. Table VIII presents the published criteria relating to mining in West Virginia and Pennsylvania.

The previous studies had shown that the stream standards of West Virginia could be met with the exception of sulfate and that the more stringent effluent standards of Pennsylvania could be satisfied. It also was evident that the iron, aluminum, and net alkalinity requirements could be met at a pH less than 6.0. Therefore, in order to meet the pH 6.0 requirement, the system must be operated at less than maximum utilization efficiency. Referring to Figure 6, it can be seen that the amounts of neutralizing agent required for an increase in pH from the optimum values given in Table VII are more for limestone and soda ash than for lime. Therefore, the limestone and soda ash neutralization efficiencies decrease at a higher rate than lime as the pH increases.

Thus our choice of operating conditions were:

-pH 6.0 to pH 6.5
-Iron removal below 7.0 ppm
-Net alkalinity (Alkalinity exceeds acidity)

Table VIII
Water Quality Criteria

State of West Virginia[6]

pH	5.5 minimum, 8.5 maximum
Iron	10 ppm
Aluminum	30 ppm
Sulfates	200 ppm

These are stream standards. There are no effluent standards in West Virginia.

Commonwealth of Pennsylvania[7]

pH	6.0 minimum, 9.0 maximum
Net Alkalinity	
Iron	7.0 ppm maximum

These are effluent standards.

Pilot Plant Studies

Actual pilot plant operation supplied the following data. These data have been evaluated and mathmatically reduced to eliminate, as much as possible, the effects of variations due to day-to-day fluctuation of water quality in Grassy Run.

Limestone: Because of the delay in the limestone treated water reaching a final pH, it was necessary for control purposes to establish a lower pH in the reactor in order to obtain the desired

resulting effluent pH. For example, for the test reported in Table IX, a pH of 5.8 was maintained in the reactor which resulted in a pH of 6.6 in the plant effluent. The pH maintained in the reactor was called the instantaneous in-reactor pH. This phenomenon causes some difficulties in operating a limestone treatment system.

Table IX

Limestone Slurry Neutralization of Grassy Run Water* - Run A

Instantaneous In-Reactor pH = 5.8**
Raw Water Feed Rate = 6,402 ml/min (1.69 gpm)
Limestone Slurry Feed Rate = 182 ml/min slurry (9.1 grams/min limestone)

Reactor Detention Time = 33 minutes (theoretical)
Settling Tank Detention Time = 12 hours (theoretical)

MEAN DATA***

Parameter	Units	Feed Water	Reactor Effluent	Settling Tank Effluent
pH (after 24 hrs)		2.9	6.6	6.6
(after 48 hrs)			6.8	6.8
(after 72 hrs)			7.1	7.0
Hot Acidity	mg/l	362	0.0	0.0
Cold Acidity	mg/l	373	33.0	25.0
Iron	mg/l	195	7.3	7.0
Sulfates	mg/l	516	479.0	479.0
Hardness	mg/l	626	1,647.0	1,547.0
Conductivity	Mmhos/cm	927	841.0	857.0
Magnesium	mg/l	171	175.0	170.0
Alkalinity	mg/l	0	78.0	66.0
Calcium	mg/l	455	1,472.0	1,377.0
Aluminum	mg/l	33	1.6	0.9
Temperature of Water		10°C	10°C	9°C
Acid Removed (Hot)	mg/l		362.0	362.0
Acid Removed (Cold)	mg/l		340.0	348.0
Limestone Utilization Efficiency			32.1%	31.2%

Lbs Limestone/1,000 gal = 11.8 lbs/1,000 gal
Chemical Cost per 1,000 gal = $0.354/1,000 gal
Chemical Cost per mg/l Acidity/1,000 gal = 0.010 cents

Percent Sludge by volume (1 hour settling time) = 3.5%
Percent Sludge by volume (24 hours settling time) = 3.7%

*All analyses made 24 hours after sampling, except as noted for pH
**pH of water in the reaction tank during the test run
***Summary of many sets of data taken during the test run.

Tables IX and X show the results of treatment of two different concentrations of Grassy Run water with "rock dust" limestone. In these instances, the limestone was introduced in the slurry form.

The cost of limestone is 1.7 times as great to treat the water in Table X as in Table IX and the water's acidity is 1.7 times as concentrated. The chemical cost was 0.010 cents per mg/l acidity per 1,000 gallons. Similarly, there is no significant difference in utilization efficiency between the two.

Lime: Table XI shows data acquired from neutralization with lime. Utilization efficiency of lime approaches 100 percent and is easily maintained, even at high pH's. Unlike limestone, the pH was slightly less in the plant effluent than in the reactor.

Supernatant water quality from lime is relatively good. However, as in the case of limestone, the water still remains typically high in hardness, calcium, and sulfates. Removal of iron with lime was better than that recorded for limestone as supernatant iron concentrations were consistently below 3.0 ppm. Better iron removal probably is partially attributable to the higher pH's attained using lime.

However, the very low percent solids of the lime sludge (1.7 percent) will be a major problem when considering sludge disposal.

Soda Ash: Table XII contains the results of the pilot plant test using sodium carbonate as the neutralizing agent.

It is seen that soda ash has only one major advantage over lime or limestone, i.e., the low hardness concentration. Utilization efficiency, as in the case of lime, approached 100 percent. However, the one major disadvantage of soda ash treatment was its higher cost. The chemical cost for treating with soda ash was 0.049 cents per mg/l acidity per 1,000 gallons treated. Soda ash treatment costs four times more than limestone and nine times more than lime.

Even though the hardness is low using soda ash, the sodium concentration was increased from 2.8 mg/l to 450 mg/l (Table XII).

Table X

Limestone Slurry Neutralization of Grassy Run Water*- Run B

Instantaneous In-Reactor pH = 5.7**
Raw Water Feed Rate = 4,800 mg/min (1.27 gpm)
Limestone Slurry Feed Rate = 228 ml/min slurry (11.4 grams/min limestone)
Reactor Detention Time = 43 minutes (theoretical)
Settling Tank Detention Time = 16 hours (theoretical)

MEAN DATA***

Parameter	Units	Feed Water	Reactor Effluent	Settling Tank Effluent
pH		2.7	6.7	6.6
Hot Acidity	mg/l	602	0	0
Cold Acidity	mg/l	595	77	79
Iron	mg/l	145	5	5
Sulfates	mg/l	904	663	723
Hardness	mg/l	588	1,621	1,588
Conductivity	Mmhos/cm	1,250	1,100	1,150
Magnesium	mg/l	188	196	188
Alkalinity	mg/l	0	122	90
Calcium	mg/l	400	1,425	1,400
Aluminum	mg/l	44	3.8	3.9
Temperature of Water		5°C	7°C	7°C
Acid Removed (Hot)	mg/l		602	602
Acid Removed (Cold)	mg/l		518	516
Limestone Utilization Efficiency			31.5%	30.1%

Lbs Limestone/1,000 gal = 19.7 lbs/1000 gal of Grassy Run Water
Chemical cost per 1,000 gal = $0.0591/1,000 gal.
Chemical cost per mg/l acidity per 1,000 gal = 0.010 cents

Percent Sludge per Volume (1 hour settling time) = 5.0%
Percent Sludge per Volume (24 hours settling time) = 4.5%

*All analyses made 24 hours after sampling.
**pH of water in the reaction tank during the test run.
***Summary of many sets of data taken during the first run.

Table XI
Lime Neutralization of Grassy Run Water*

Instantaneous In-Reactor pH = 7.9**
Raw Water Feed Rate = 5,964 mg/l (1.58 gpm)
Lime Feed Rate = 2.69 grams/min
Reactor Detention Time = 35 minutes (theoretical)
Settling Tank Detention Time = 13 hours (theoretical)

MEAN DATA***

Parameter	Units	Feed Water	Reactor Effluent	Settling Tank Effluent
pH	mg/l	2.8	7.1	6.9
Hot Acidity	mg/l	601	2.1	1.7
Cold Acidity	mg/l	612	0.4	2.6
Iron	mg/l	157	2.4	1.6
Sulfates	mg/l	717	709	693
Hardness	mg/l	582	1,261	1,220
Conductivity	Mmhos/cm	1,450	1,241	1,245
Magnesium	mg/l	135	162	145
Alkalinity	mg/l	0	17	11
Calcium	mg/l	447	1,099	1,075
Aluminum	mg/l	33	0.8	0.9
Temperature of Water		13°C	15°C	15°C
Acid Removed (Hot)	mg/l		599	599
Acid Removed (Cold)	mg/l		612	609
Lime Utilization Efficiency			103%	102%

Lbs Lime/1,000 gal = 3.75 lbs/1,000 gal of Grassy Run Water
Chemical cost per 1,000 gal = $0.032/1,000 gallons of Grassy Run Water
Chemical cost per mg/l acidity/1,000 gal = 0.0052 cents

Percent sludge by Volume = 6.9% (24 hours settling)
Percent solids in sludge = 1.7%

*Chemical analyses made 24 hours after sampling.
**pH of water in the reaction tank during the test run
***Summary of many sets of data taken during the test run.

Table XII
Soda Ash Neutralization of Grassy Run Water*

Instantaneous In-Reactor pH = 6.0**
Raw Water Feed Rate = 11,000 ml/min or 2.91 gpm
Soda Ash Feed Rate = 7.1 grams/min
Reactor Detention Time = 19 minutes (theoretical)
Settling Tank Detention Time = 7.2 hours (theoretical)

MEAN DATA***

Parameter	Units	Feed Water	Reactor Effluent	Settling Tank Effluent
pH		2.7	6.1	6.5
Hot Acidity	mg/l	551	0	0
Cold Acidity	mg/l	586	73	0
Iron	mg/l	126	7.9	2.3
Sulfates	mg/l	581	540	546
Hardness	mg/l	526	530	541
Conductivity	Mmhos/cm	1,300	1,425	1,500
Magnesium	mg/l	205	205	208
Alkalinity	mg/l	0	100	103
Calcium	mg/l	321	325	333
Aluminum	mg/l	41	3.5	2.2
Sodium	mg/l	2.8	555	450
Temperature of Water		12°C	12°C	12°C
Acid Removed (Hot)	mg/l		551	551
Acid Removed (Cold)	mg/l		513	586
Soda Ash Utilization Efficiency			106.8%	107.3%

Lbs Soda Ash/1,000 Gallons = 5.367 lbs/1,000 gallons of Grassy Run Water

Chemical cost per 1,000 gallons = $0.268/1,000 gallons of Grassy Run Water

Chemical cost per mg/l acidity/1,000 gal = 0.0486 cents

Percent Sluoge by Volume = 7.6% (24 hours settling)
Percent Solids in Sludge = 1.5%

*Chemical analyses made 24 hours after sampling.
**pH of water in the reaction tank during the test run.
***Summary of several sets of data taken during the test run.

DISCUSSION OF RESULTS

In Table XIII, the changes in water quality due to neutralization with lime, limestone, and soda ash are summarized. Small differences between the neutralization agents are due to differences in the water quality during the period the pilot plant was in operation. In essence all three agents were capable of reducing the acidity and iron, and increasing the alkalinity and pH to the Pennsylvania criteria (Table VIII). The aluminum was also significantly reduced. As would be expected, the calcium and magnesium increased when lime and limestone was used and sodium when soda ash was used.

Table XIII
Effects of Neutralization with
Lime, Limestone, and Soda Ash on Water Quality*

Parameter	Lime	Limestone	Soda Ash
Acidity(Hot)	Reduced 99.7%	Reduced 100.0%	Reduced 100.0%
Acidity(Cold)	Reduced 99.5%	Reduced 90.0%	Reduced 100.0%
Iron	Reduced 99.0%	Reduced 96.2%	Reduced 98.2%
Sulfates	Reduced 3.3%	Reduced 13.6%	Reduced 6.0%
Hardness	Increased 209.6%	Increased 258.5%	Increased 2.8%
Conductivity	Reduced 14.1%	Reduced 7.8%	Increased 15.4%
Alkalinity	Increased to 11 mg/l	Increased to 78 mg/l	Increased to 103 mg/l
Calcium	Increased 240.5%	Increased 310.5%	Increased 3.7%
Aluminum	Reduced 97.3%	Reduced 94.2%	Reduced 94.6%
Magnesium	Increased 107.4%	Increased 141.8%	Increased 101.5%
Sodium			Increased to 450 mg/l

*Lime treated water was raised to pH 6.9, limestone 6.6, and soda ash 6.5

A comparison of the relative settling rates between lime, limestone, and soda ash sludges are presented in Figure 7. Sludge from the limestone reaction compacts to the smallest volume and settling is completed in approximately one hour. Lime sludge has a very rapid initial settling rate (due to the rapid lime reaction and attainment of higher pH) but suffers from poor compaction. It requires almost five times as long for the lime to reach a state of final compaction as for the limestone. However, better than 90 percent of the total settling is completed in less than one hour. The soda ash settling characteristics are virtually identical to those of the lime.

A test was made to compare the percent sludge solids of lime, limestone, and soda ash sludges. Using the same water, samples were neutralized

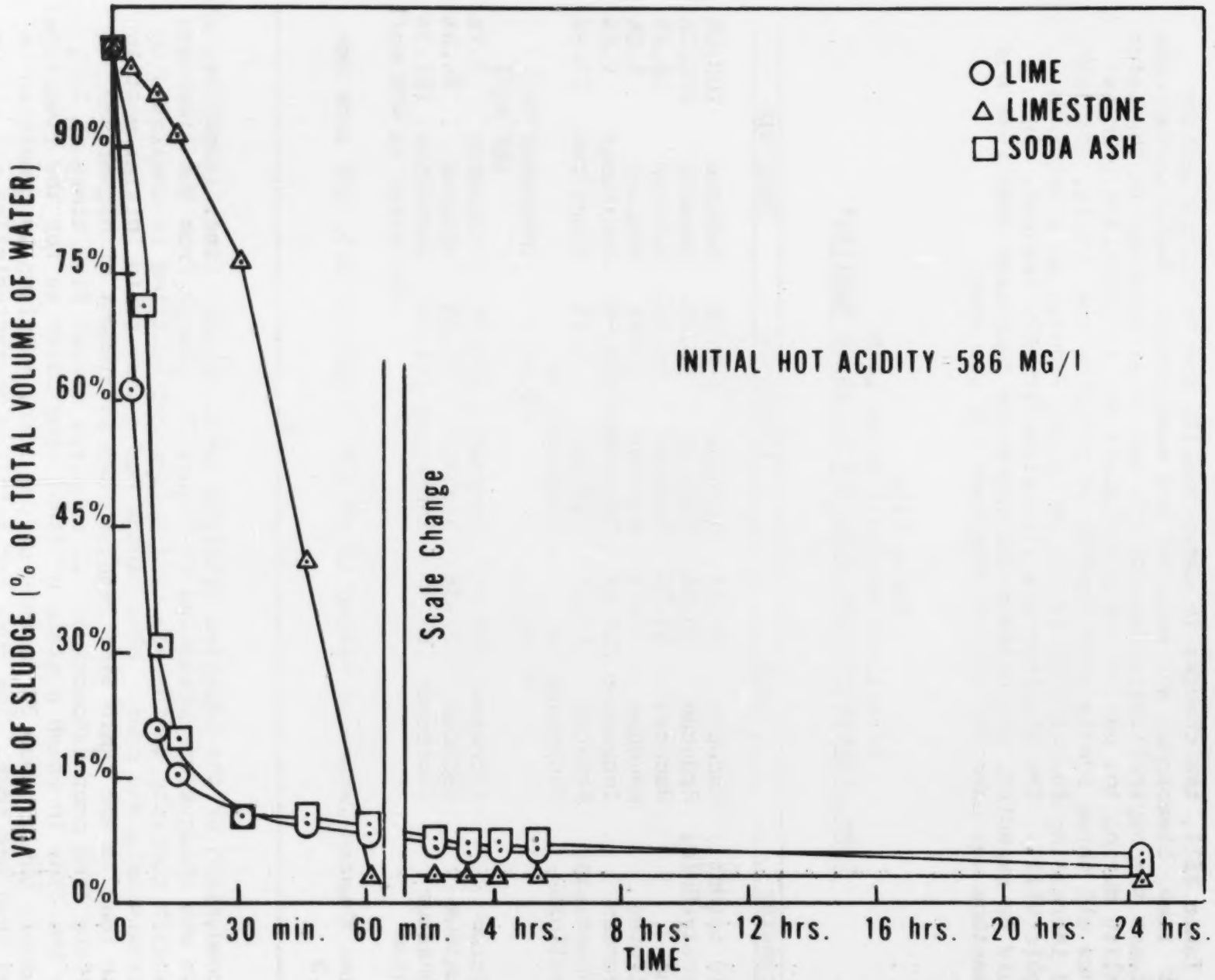

FIGURE 7 COMPARISON OF SETTLING RATE

to pH 6.5 (lime and soda ash) and pH 6.2 (limestone) allowed to settle 24 hours and then the sludge was withdrawn and percent solids determined. Table XIV presents the results of these tests. Limestone sludge contained a higher solids content.

Table XIV
Percent Solids of Sludges*

Neutralizing Agent	Supernatant pH	Percent Solids of Sludge
Lime	pH 6.5	1.5%
Limestone	pH 6.2	9.5%
Soda Ash	pH 6.5	0.7%

*After 24 hours of undisturbed settling

Lime and limestone settling tests were also run on a Grassy Run water sample which had been concentrated 3.3 times by a reverse osmosis unit. The results of this test on the concentrated water are presented in Figure 8. Comparing the results for this water as opposed to the unconcentrated Grassy Run water, it was found that the general settling trend of lime did not appear to vary with increased concentrations. In the case of limestone, marked improvements in settling characteristics were apparent in the concentrated water. In both cases over 90 percent of the settling was completed in one hour. The sludge volumes were greater for the concentrated water than for the mine drainage due to the larger amounts of iron, calcium and etc., that were available for precipitation.

In Table XV, the chemical cost for treating acid mine drainage by the three neutralizing agents is summarized. The cost figures calculated as cents per mg/l acidity per 1,000 gallons are most representative because they account for the difference in the acidity of the mine drainage during the test run and are comparable to other neutralization studies. This type of comparison has been made for two studies reported in the literature and are reported below.

Table XV
Chemical Cost for Treating Acid Mine Drainage

	Dollars per 1,000 gallons	Cents per mg/l acidity per 1,000 gallons
Lime	0.032	0.005
Limestone	0.035 - 0.059	0.010
Soda Ash	0.268	0.049

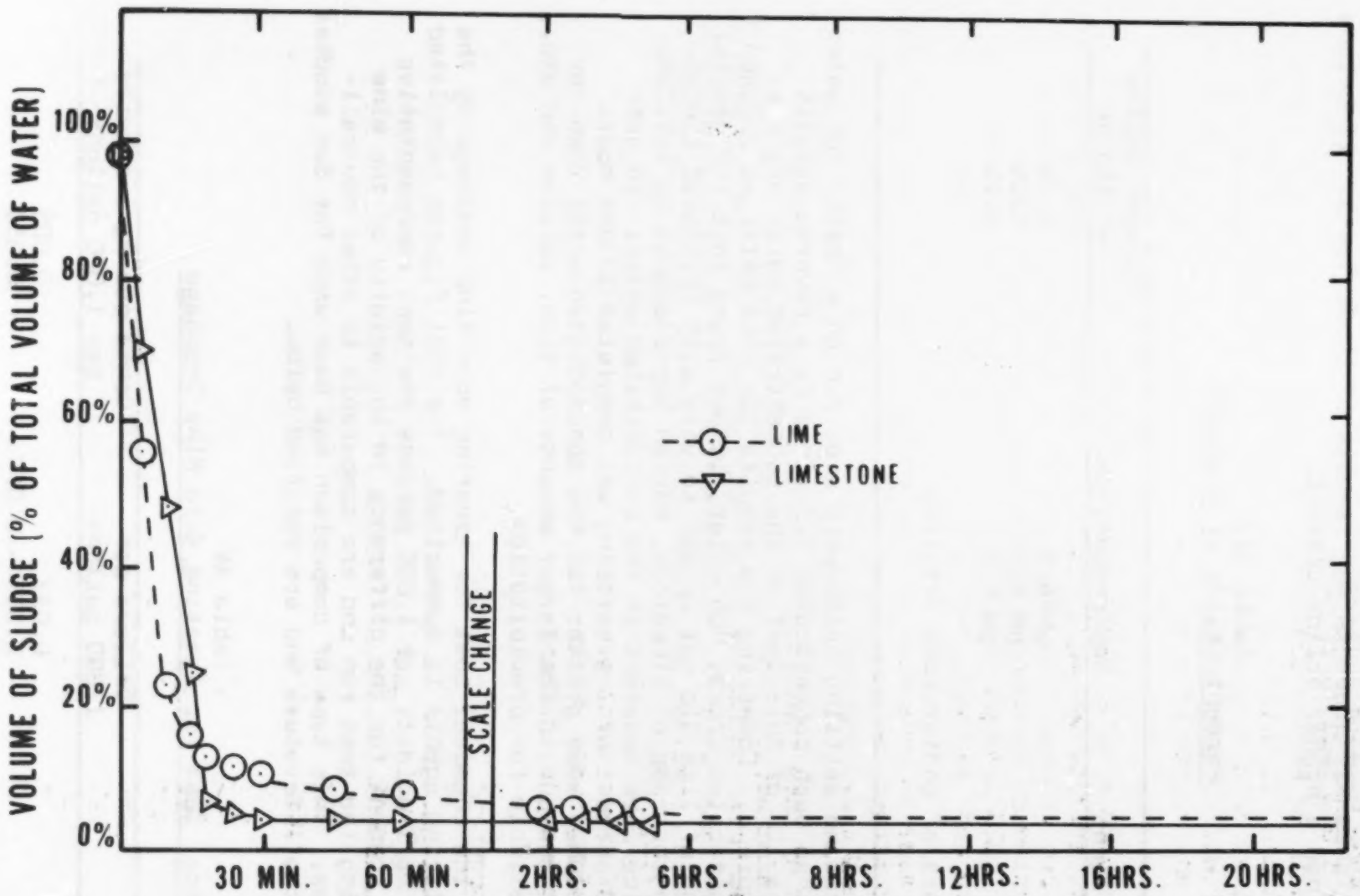

FIGURE 8

COMPARISON OF SETTLING RATE
BETWEEN LIME AND LIMESTONE NEUTRALIZATION

Corsaro, Holland, and Ladish[9], of West Virginia University, reported the chemical cost of lime treating water comparable to Grassy Run was 6.1 cents per 1,000 gallons of water treated. Recalculating this figure on the basis of Norton lime cost, their cost would be 4.7 cents per 1,000 gallons, or 0.0072 cents per mg/l acidity per 1,000 gallons. Thus the cost at West Virginia University was 0.0019 cents per mg/l acidity per 1,000 gallons higher. This cost difference is attributed partially to the higher pH's to which West Virginia University raised their water.

Calhoun[8] treated a water similar to Grassy Run, (total iron 68 mg/l, mostly ferric, acidity 345 mg/l), using limestone and reported somewhat better iron removal than was achieved in this study. Limestone costs were estimated by Calhoun to approach one cent per 1,000 gallons, or a cost of 0.003 cent per mg/l acid/1,000 gallons was obtained, compared to 0.010 cent per mg/l per 1,000 gallons for this study.

Studies were made to determine if the method of neutralizing agent additions would affect the results of the neutralizing agents. Dry feed and slurry feed were compared.

Equal amounts of each neutralizing agent were added to identical samples of acid mine water. The only difference was that one was slurried with distilled water while the other was fed dry. The samples were then agitated by a flash mixer for five minutes and the suspended solids allowed to settle. Analyses were made on all samples at an identical time after mixing.

The results of these tests are presented in Table XVI and indicate there is no significant difference in water quality or utilization efficiency between dry feeding or slurry feeding.

Table XVI
Comparison of Dry Feeding and Slurry Feeding

	Raw Water	Lime		Limestone		Soda Ash	
		Dry	Slurry	Dry	Slurry	Dry	Slurry
pH	2.7	6.1	6.2	6.6	6.8	6.8	6.8
Conductivity	1,650	1,460	1,460	1,460	1,460	1,750	1,750
Hot Acidity	532	0	0	0	0	0	0
Cold Acidity	558	69	64	90	12	65	24
Calcium	318	812	812	862	844	318	300
Magnesium	212	212	212	206	206	214	201
Hardness	530	1,024	1,024	1,068	1,050	532	501
Sulfates	868	747	723	723	688	723	699
Iron	120	2.3	2.0	2.1	2.2	4.9	6.3
Aluminum	35	1.1	1.2	1.3	1.2	2.7	2.4
Alkalinity	0	17	18	50	50	97	91
Sodium	2	2.3	2.2	2.0	2.0	380	320

All units are mg/l except for conductivity (Mmhos/cm)and pH.

The studies up to this point had shown limestone to have several advantages, e.g., the raw material cost was $17.00 per ton for lime and $6.00 per ton for limestone and the sludge from limestone treatment was less voluminous and more dense. On the other hand, the utilization efficiency was only 32 percent for limestone and 100 percent for lime. Based on the utilization efficiency, it would appear that three times as much limestone as lime would be needed to treat the same water. Thus, the cost of treating with limestone would appear to be 1.1 times more than with lime.

However, utilization efficiency is a measure of the ratio of the acidity removed and alkalinity added to the water to the alkalinity added in the neutralizing agent and cannot be used to compare two different neutralizing agents. First, a pound of lime does not contain the same alkalinity as a pound of limestone, as a pound of lime is equal to 1.35 pounds of limestone. Also, whereas lime is a pure neutralizer, limestone is not (only 96.5 percent in this study) and thus, even more limestone is required. Secondly, the utilization efficiency gives credit to the alkalinity added to the water whereas, on a cost basis alone, this alkalinity is a waste of material and can increase cost. Since more alkalinity was added to the water by limestone than by lime (Table XIII) the cost of limestone treatment is that much higher. Table XV presents the actual cost difference.

In order to have limestone compete with lime, cost wise, it is necessary to improve the efficiency of the limestone process. Several methods were initially conceived: 1. Increase the detention time of the water in the reactor, thus,providing time for more limestone to become solubilized. 2. Increasing of the vigorous mixing action in the reactor to create more complete breakdown of the limestone, as earlier studies indicated the more rapid the mixing, the better the results. 3. Return the sludge with its unused limestone back to the reactor, and 4. Aerate the water to strip off the carbon dioxide and thereby reduce the buffering capacity.

The test equipment on hand was unsuitable to perform tests on items two and three, so a new and larger test facility has been constructed to study these factors. Item number one could not be studied directly with the present equipment. However, studies in comparing dry feed and slurry feed gave some indirect light. Aeration was studied as part of the current study.

First attempts at aeration were performed in the upflow settling tank. The data are presented in Table XVII. The effluent pH rose immediately from pH 6.7 to pH 7.1 as soon as aeration began. However, cold acidity barely dropped (from 29 mg/l to 25 mg/l) and the overall rise in efficiency was 0.9 percent. This insignificant change certainly does not justify aeration.

Aeration in the reactor was then studied. (Table XVIII). A more pronounced pH change occurred after aeration (from pH 6.3 to pH 7.0) and the cold acidity was reduced 25 percent. However, product alkalinity

was reduced 34 percent, thus resulting in a 1.6 percent net loss in efficiency. There were no other significant changes in overall water quality.

In summary, aeration of the limestone reaction proved to be of no value in increasing efficiency. However, as it rapidly strips off CO_2, it could be very useful in drastically reducing detention time before supernatant discharge (discharge occurs when desired pH is attained) and would be especially applicable at sites were installation or presence of large holding lagoons (for the purpose of detention time) would not be feasible.

Table XVII
Grassy Run - Slurry Feed Limestone
Comparison of Data Prior to and During
Aeration of Settling Tank

Instantaneous In-Reactor pH = 6.5*

Parameter	Units	Feed Water	Before Aeration Settling Tank	Aeration Settling Tank
pH	mg/l	2.9	6.7	7.1
Hot Acid	mg/l	375	0	0
Cold Acid	mg/l	379	29	25
Iron	mg/l	185	2.5	3.1
SO_4	mg/l	542	506	544
Hardness	mg/l	564	1,375	1,263
Conductivity	Mmhos/cm	1,100	1,100	1,100
Alkalinity	mg/l	0	72	87
Calcium	mg/l	394	1,219	1,103
Aluminum	mg/l	30	0.7	0.5
Flow Rate (Mean)	1.48 gpm	208 ml/min limestone slurry		
	5,600 ml/min	10.4 grams/min limestone		
Acid Removed (Hot)	mg/l		375	375
Acid Removed (Cold)	mg/l		350	354
Limestone Utilization Efficiency			24.0%	24.9%

Chemistry analyses made 24 hours after samples were taken.
Data from settling tank represent five samples taken within four hours after aeration was started.

*pH of water in the reaction tank during the test run.

Table XVIII
Comparison of Aeration and Non-Aeration of Reactor

Instantaneous In-Reactor pH = 6.5*
Flow Rate Feed Water = 6,867 ml/min
Flow Rate Limestone Slurry = 205 ml/min
Temperature of Water = 18° C

		Non-Aeration			Aeration		
		Feed	Effluent		Feed	Effluent	
Parameter	Units	Water	At 1 Hr.	At 24 Hrs.	Water	At 1 Hr.	At 24 Hrs.
pH		2.8	6.3	7.0	2.8	7.0	7.3
Hot Acid	mg/l	464	0	0	454	0	0
Cold Acid	mg/l	470	41	16	472	30	9
Iron	mg/l	136	23	7.9	139	20	4.3
SO_4	mg/l	591	566	530	486	466	542
Hardness	mg/l	439	1,184	1,168	452	1,263	1,360
Conductivity	Mmhos/cm	1,200	1,000	1,000	1,167	973	967
Alkalinity	mg/l	0	56	62	0	41	45
Calcium	mg/l	300	1,044	1,031	310	1,113	1,200
Aluminum	mg/l	30.8	5	2.2	34	5.0	1.6
Acid Removed (Hot)	mg/l		464	464		454	454
Acid Removed (Cold)	mg/l		429	454		442	463
Limestone Utilization Efficiency			34.8%	35.2%		33.2%	33.4%

*pH of water in the reaction tank during the test run.

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All three neutralizing agents were capable of treating acid mine drainage. Lime costs were half that of limestone

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for treating the same acid mine drainage because of the low utilization of limestone. However, the characteristics of the limestone sludge were superior to those of lime and soda ash sludges. The cost for soda ash treatment was excessive. Further research on improving limestone utilization is under way.

No differences in reaction efficiency were found in dry feeding or slurry feeding the neutralizing agents.

Aeration during and/or after the limestone reaction merely increased the effluent pH but failed to increase limestone useage efficiency or improve the effluent quality.

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